CHEMICAL DESULFURIZATION OF COAL: PARTITIONING SULFUR TO GAS AS H_2S

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INTRODUCTION

The yields and characterisitics of products from mild temperature gasification or pyrolysis of coal have been evaluated extensively in fundamental and process development efforts. At 500°C, the following has been presented as representing the sulfur product distribution from US bituminous coals (1,2):

$$\text{Total sulfur in gas} = 0.31 \times S_{coal}$$
$$\text{Total sulfur in tar} = 0.06 \times S_{coal}$$
$$\text{Total sulfur in solid} = 0.61 \times S_{coal}.$$

This type of distribution is affected by factors such as coal type, sulfur content and form, particle size, heating rates, temperature of pyrolysis, reactor and process design, and the type of reactants to which the coal is subjected. For example, increasing the pyrolysis residence time usually decreases the sulfur content in the char and increases the tar and gas yields and their sulfur content.

As indicated above, and in other mild temperature gasification studies of low-to-high sulfur coals at temperatures between 400-825°C (3-5), the coal sulfur was distributed nonselectively to all products. As a consequence, the upgrading required to meet environmental regulations has to be applied to more diverse products than the coal from which the products were derived. The severity of such upgrading, and the severity to which coal has to be treated to release all of its sulfur, depends on the chemical form of the sulfur. Recent analytical efforts have begun to define these sulfur forms in coal, the most refractory organic species of which are thiophenic in nature (6,7).

In the current study, the mild temperature pyrolysis of Illinois basin coals mixed with phosphoric acid under continuous-feed, bench-scale fluidized bed conditions at 500°C is reported. The extent of sulfur removal and its partitioning to gas as H_2S are discussed in relation to its chemical form in the coal. Swelling characteristics of coal/acid mixtures are also discussed relative to operation of the fluidized bed reactor.

EXPERIMENTAL

The two coal samples (labelled as VA and VB) were obtained from the Illinois Basin Coal Sample Program and were both from the Springfield seam (Indiana V), but were sampled at different locations in the seam and at different times. Their composition is presented in Table 1.

The coals were admixed with 50% strength, reagent grade phosphoric acid to attain coal:acid weight ratios of 1.0:0.65 and 1.0:0.96 or with water to produce a coal-only sample having a coal:acid ratio of 1.0:0. These mixtures were dried at 200°C in a nitrogen purged furnace then vacuum dried at the same temperature. The dried samples were stored in sealed containers subsequent to purging with argon until they were treated in a bench-scale reactor.

A schematic of the fluidized bed reactor system is presented in Figure 1. The reactor had a 7.6 cm diameter and was 100 cm in height. Dried coals were loaded into a pressurized hopper located on a precision screw feeder. Coal was dropped from the screw outlet of the feeder into a eductor line which led to the bottom of the gasifier. Gasification tests were as long as four hours in duration with average coal feeds of 0.1-0.3 kg/h.

Nitrogen, nitrogen/air or nitrogen/steam were used as the fluidizing gas during pyrolysis. These gases were pre-heated in a furnace upstream from the fluid bed. Heat traced lines were used to maintain constant temperatures throughout the reactor and its associated output streams. Chars were collected in the down-leg of a cyclone and in an underbed collection flask. A three-stage condensate collection system was used, with the first stage at 140°C, the second stage at 15°C, and the third stage at 0°C.

Subsequent to pyrolysis and before analysis, the chars were hot water filtered to remove excess phosphorus. For these experiments, a stainless steel, 1.4 l pressure filter (Model KST, Lars Lande Manufacturing, Inc.) was insulated and connected to an in-line water heater, a flow meter and a pump.

RESULTS AND DISCUSSION

Product yields for the two coals were repeatable and similar. On a maf basis, and calculated from (weight feed - weight product)/weight feed, the char yields were near 65% for either 1.0:0.96 or 1.0:0.65 parent coal:acid ratios, and between 70-80% for the same acid ratios when treating physically cleaned coals. These numbers are to be compared with char yields near 60% for coals without added phosphoric acid. The tar yields varied between 0.5-1.5% for coal:acid feeds and near 5% for coal-only feeds. Increasing the phosphoric acid concentration decreased significantly the tar yields.

The duration of the pyrolysis tests using coal-only feeds was slightly greater than one hour, whereas for coal:phosphoric acid feeds the test durations were greater than 2.5 hours. This difference was solely a consequence of difficulties in operating the fluidized bed reactor. For coal-only, agglomeration of the coal in the bubbling bed caused defluidization and bed blockage, and accumulation of tar at the air-side outlet of the cyclone caused pressure increases within the pyrolysis zone and, eventually, bed blockage. Relative to the swelling character of the feed coal, the free swelling index (FSI) was 3.4 whereas the FSI of a 1.0:0.96 mixture was less than one. Previous work examined the effects of HCl on the swelling character of coals (8,9); the present data indicate that phosphoric acid also greatly affects coal thermoplastic properities.

Data presented in Table 1 show the composition of chars produced from the two coals with and without phosphoric acid. Approximately 20% of the sulfur originally in the coals remained in the chars after the 500°C fluidized bed testing of coal:acid mixtures, whereas nearly 70% of the sulfur remained in the char after pyrolysis of coal-only samples. About 90% of the sulfur remaining in the char produced from coal:acid mixtures was organic in nature. The sulfur in the tars accounted for less than 1% of the total amount of sulfur originally in the coals, whereas over 75% of the coal sulfur was selectively partitioned to the gas phase as H_2S.

Char yields were greater for the coal:acid ratio of 1.0:0.65 than for the 1.0:0.96 ratio, and sulfur removal was increased with increasing acid concentration. This behavior may be a result of competition between alkylating and polymerization functions of phosphoric acid, in combination with the influence of creating char porosity during gasification. For example, the BET N_2 surface area of the char from VA was 445 m^2/g when using the 1.0:0.96 coal:acid ratio whereas it was 177 m^2/g when using the 1.0:0.65 ratio. The extent to which sulfur can be removed from coal during hydropyrolysis has been attributed, in part, to the development of porosity (8). In addition, an increased rate of heating during gasification or pyrolysis influences the softening, swelling and shrinking properties of the coals, and changes significantly the porosity of the char. However, phosphoric acid treatment does not increase the concentration of oxygen in the chars relative to that in the coals.

The amount of sulfur removed from coal:acid mixtures was significantly greater than the amount of sulfur removed from coal-only feeds. The extent to which sulfur was removed is similar to that observed in fixed-bed testing using coal:phosphoric acid mixtures (10), although in the current case the mean residence time of the coal within the reactor was on the order of minutes rather than hours.

Practically total elimination of the pyritic sulfur occurred for all coal:acid mixture feeds. It was also observed that this elimination could be facilitated at temperatures as low as 200°C - i.e. during the initial drying/evacuation before fluidized bed treatment at 500°C. Hence, phosphoric acid decreases the temperature at which pyrite decomposition is initiated. In comparison to the sulfur distribution shown above, which is typical of that obtained during mild temperature gasification, the pyrolysis of coal:phosphoric acid under the same conditions produced the following distribution:

$$\text{Total sulfur in gas} \sim 0.80\ S_{coal}$$
$$\text{Total sulfur in tar} \sim 0.01\ S_{coal}$$
$$\text{Total sulfur in char} < 0.20\ S_{coal}.$$

The form of the sulfur which remained in the Indiana V chars is not known. However, the chemical form of sulfur species in Indiana V coal has been investigated by XANES spectroscopy (11). Even though this XANES-investigated sample was oxidized, about 16% of its sulfur could be identified as a thiophenic species. Such a value is in close agreement with the amount of sulfur remaining in the chars from coal:acid mixtures. Hence, the sulfur in the chars may be predominantly thiophenic species.

Phosphorus remaining in the char after pyrolysis can be removed by hydrolysis since there is reversibility between orthophosphoric acid (H_3PO_4) and the pyrophosphoric form ($H_2P_2O_7$) and more polymeric metaphosphate forms. Such removal and the sulfur partitioning suggests a coal utilization scheme as depicted in Figure 2. It would produce valuable elemental sulfur or sulfuric acid from the gas phase H_2S, minimize byproducts formation, and integrate with advanced topping combustor cycles.

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Table 1. Composition of Indiana V coals (sample A and B) and chars produced during 500°C, fluidized bed pyrolysis.

	COALS		1.0:0.96 RATIO*		COAL-ONLY
ANALYSIS(%)	VA	VB	CHAR A	CHAR B	CHAR B'
Moisture	6.16	5.48	1.88	4.88	3.84
Ash	7.14	8.65	23.61	21.25	10.54
Vol. Mat.	38.37	40.09	22.45	21.54	20.93
Fixed C.	48.30	45.80	52.01	52.22	64.70
Carbon	69.29	67.87	66.77	66.78	74.28
Hydrogen	5.49	5.46	1.86	2.52	3.10
Nitrogen	1.47	1.42	1.61	1.36	1.70
Sulfur	3.45	3.95	0.81	0.95	2.64
Pyritic S	1.50	1.40	0.13	0.18	-
Organic S	1.95	2.51	0.66	0.70	-
Sulfatic S	0.01	0.04	0.02	0.04	-

*1.0:0.96 = Coal:Acid Ratio (see text).

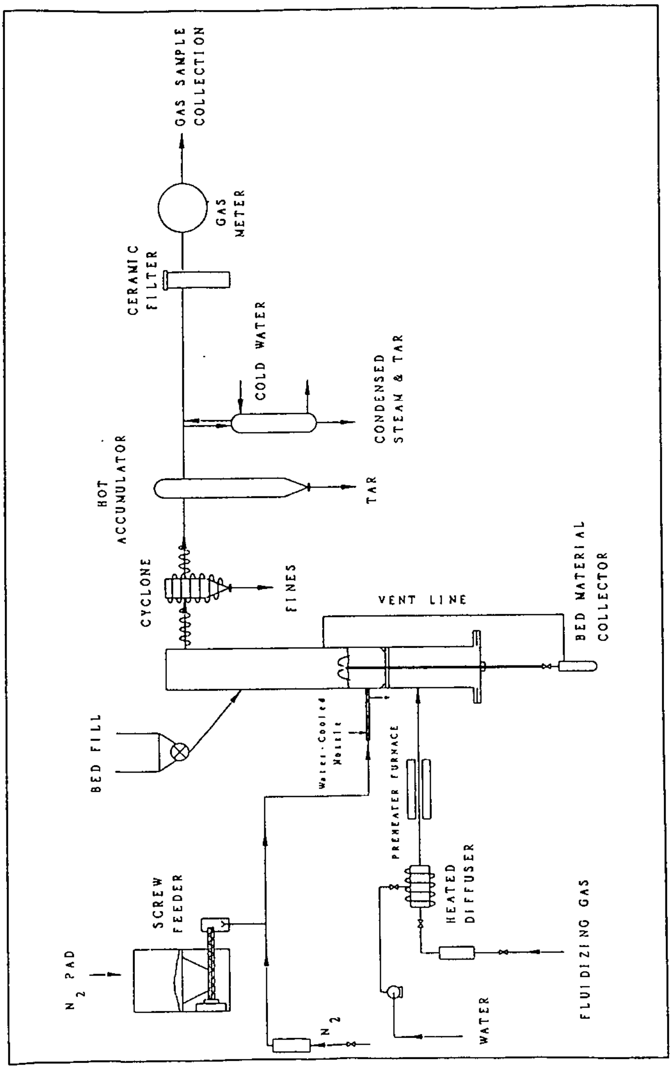

Figure 1. Experimental system used to pyrolyze coal and coal:phosphoric acid mixtures under fluidized bed conditions.

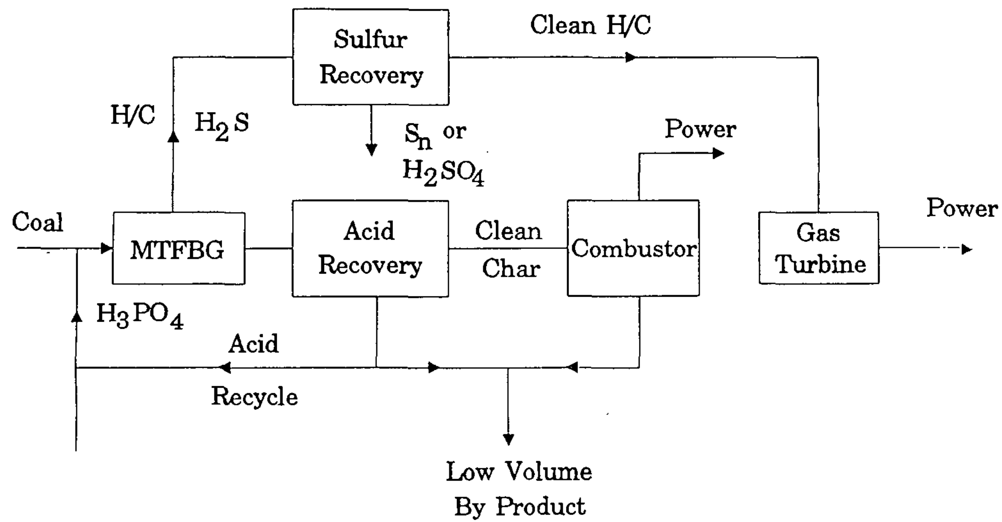

Figure 2. Proposed process using coal:phosphoric acid mixtures.